isomers of 1,3-disubstituted cyclohexanes have the higher refractive indexes and the higher densities. According to this, the data of Table 1 indicate the *cis* structure for isomers (A) and (C), and the *trans* structure for (B) and (D). These assignments agree with the relative rentention times of isomers (A) and (C), as the *cis* isomers usually has shorter retention time than the *trans* isomer. The structural relationship of the two *cis-trans* pairs are at present being further investigated.

Experimental. 5-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (III). Triethyl phosphite (50 g) and 2-methyl-1,4-dibromobutane (20 g) were stirred for 2 h at 180°C. The ethyl bromide was continuously distilled off, and the remaining reaction mixture fractionated *in vacuo* in a heated jacket column to give 6.2 g (40 %), b.p.$_2$ 130°, n_D^{20} 1.4588. (Found: C 47.06; H 8.50; E 177.5. Calc. for $C_7H_{10}O_3P$: C 47.20; H 8.43; E 178.2).

6-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinan (IV) was synthesized from triethyl phosphite (50 g) and 1,4-dibromopentane (20 g) using the same procedure as above. 4.7 g (30 %), b.p.$_{0.5}$ 95°, n_D^{20} 1.4496. (Found: C 46.94; H 8.36; E 176.1. Calc. for $C_7H_{15}O_3P$: C 47.20; H 8.43; E 178.2).

GLC purity of III and IV > 99 %. The isomers were separated by means of an Aerograph Autoprep A-700 gas chromatograph using a 20′ × 1/4″ column containing 10 % PDEAS on Fluoropak 80, at 185°, and with a helium flow of 40 ml/min. GLC purity of the isomers was above 99 %.

1. Garner, A. Y. *U. S. Patent* 2953591; *Chem. Abstr.* **55** (1961) 5346.
2. Aksnes, G. and Bergesen, K. *Acta Chem. Scand.* **20** (1966) 2508.
3. von Auwers, K. *Ann.* **420** (1920) 84.
4. Skita, A. *Ber.* **56** (1923) 1014.
5. Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw, New York 1962, p. 216.

Received January 13, 1967.

Some Comments on a Reported Quinuclidine Synthesis

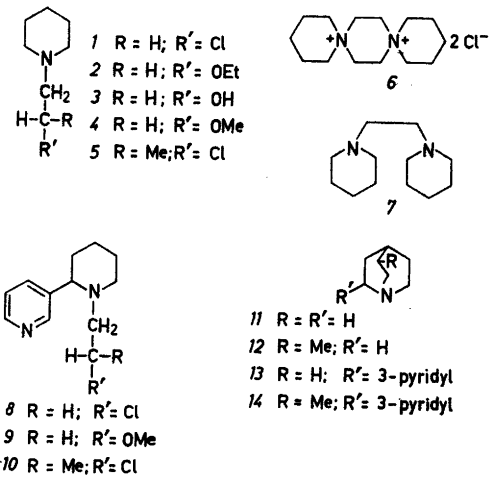
F. HAGLID

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

In the beginning of this century Knorr [1] and even others carefully investigated the chemical behaviour of tertiary β-chloroethylamines like *N*-(β-chloroethyl)-piperidine, *1*. Knorr found that compound *1* in ethanol partly dimerizes to the bis-quaternary salt *6* and partly yields the ether *2*. He found further that Hofmann cleavage of *6* effected with aqueous potassium hydroxide yields dipiperidinoethane, *7*, piperidinoethanol, *3*, and acetylene.

In 1963 Sadykov and coworkers reported the formation of quinuclidine,[2] *11*, from compound *1* by treatment with methanolic potassium hydroxide and in a second paper [2] an analogous formation of the quinuclidine derivative *13* from compound *8* by the same base treatment. In 1964 these authors, in an extention of the previous work, reported [3] an analogous formation of compounds *12* and *14*, when the corresponding β-chloropropylamines *5* and *10*, respectively, were used as starting materials.

In 1965 Rubtsov and coworkers [4] published a paper titled "Hofmann cleavage of 6,9-diazoniadispiro-(5.2.5.2.)hexadecane dichloride (compound *6*) with methanolic



potassium hydroxide", which describes a reinvestigation of Sadykov's first paper.[2] Rubtsov realized that compound *1*, described by Sadykov as a high melting solid, was in fact identical with compound *6*. As might have been expected the change of solvent to methanol (*cf.* Ref. 1) in the Hofmann degradation of compound *6* had no marked effect on the outcome of the reaction; the main product was still compound *7* together with minor amounts of compound *4* and piperidine.

Some results obtained during a recent investigation (*cf.* Ref. 5) caused me to repeat the experiment described in Sadykov's second paper.[2] The free base *8*, an oil, seemed fairly stable and showed less tendency to dimerize than did compound *1*. Thus on treatment of *8* with methanolic potassium hydroxide, ether formation could be expected to occur as the main reaction in analogy with Knorr's findings.[1] In fact, compound *9*, *N*-(β-methoxyethyl)-anabasine, was obtained in about 80 % yield. B.p. 100°/0.1 mm (bath temp.). IR: (instruments and technique used in IR and NMR: *cf.* Ref. 5) 2820 (m) and 1120 (s, broad) cm^{-1}. NMR: three-proton singlet at δ 3.15 ppm). For comparison compound *9* was prepared independently by alkylation of anabasine with β-methoxyethyl *p*-toluenesulphonate. Identity was confirmed by GLC, IR, and a mixed melting point determination of the picrates (m.p. and mixed m.p. 174–175°).

The experiments described in Sadykov's last paper [3] have not been repeated. It must, however, be considered unlikely that the products described possessed structures *12* and *14*. As primary structural evidence Sadykov used a comparison of the IR spectrum of the alleged product *11* (actually structure *7*) with that of *12* as well as that of *13* (actually structure *9*) with *14*.

This investigation was supported by a grant from *Svenska Tobaks AB*.

1. Knorr, L., Hörlein, H. and Roth, P. *Ber.* **38** (1905) 3136, 3141.
2. Sadykov, A. S., Karimov, M. and Aslanov, Kh. A. *Zh. Obshch. Khim.* **33** (1963) 3414, 3417; [*J. Gen. Chem. USSR (Eng. Transl.)* **33** (1963) 3342, 3345].
3. Sadykov, A. S., Karimov, M. and Aslanov, Kh. A. *Zh. Obshch. Khim.* **34** (1964) 4104; [*J. Gen. Chem. USSR (Eng. Transl.)* **34** (1964) 4163].
4. Rubtsov, M. V., Yakhontov, L. N. and Mikhlina, E. E. *Zh. Obshch. Khim.* **35** (1965) 621; [*J. Gen. Chem. USSR (Eng. Transl.)* **35** (1965) 624].
5. Haglid, F. *Acta Chem. Scand.* **21** (1967) 580.

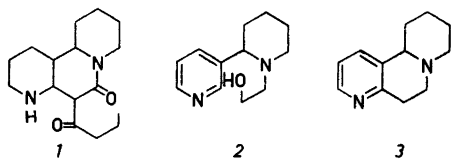
Received January 23, 1967.

Synthesis of Tricyclic Homologues of 1,6- and 2,7-Naphthyridine

F. HAGLID

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

Hydrogenated pyrrolo- and pyrido-naphthyridines of the types represented by the structural formulae *7*, *11*, and *15* were required for pharmacological investigations (*cf.* Ref. 1). Recently the alkaloid haloxine [2,3] was found to possess structure *1* embodying the skeleton *7*.



1 *2* *3*

Fig. 1.

It has been claimed [4] that a compound supposed to possess structure *3* is formed simply by heating the alcohol *2* with phosphorus pentoxide.

I have repeated this experiment but except for intractable resins only small amounts of unchanged starting material could be isolated. After several other attempts to synthesise compounds of type *7*, *11*, and *15* the reactions summarized in Scheme 1 led to the required bases.

The aminoethylpiperidines *4*, *8*, and *12*, obtained by catalytic hydrogenation of the corresponding piperidino- and pyrrolidino-ethylpyridines,[5] were methylated to compounds *5*, *9*, and *13*, respectively. When these tertiary diamines (*5*, *9*, and *13*) were oxidized with mercuric acetate,[6] mercurous acetate was formed in amounts roughly